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DEGRADATION OF HIGH ALUMINA BRICKS IN STEELMAKING LADLES

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DEGRADATION OF HIGH ALUMINA BRICKS IN STEELMAKING LADLES

by

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ABSTRACT

Slag corrosion resistance of 6-inch and 7-inch high alumina bricks was examined. The difference in degradation rate of these bricks in the steelmaking ladles was sought in terms of microstructural, chemical and physical characteristics.

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DÉGRADATION DES BRIQUES À HAUTE TENEUR EN ALUMINE DES POCHES DE COULÉE SERVANT À LA FABRICATION DE L'ACIER

par

K.E. Bell* et D.H.H. Quon**

RÉSUMÉ

On a vérifié la résistance à la corrosion due aux scories de briques de 6 et 7 pouces à haute teneur en alumine. La différence en ce qui concerne le taux de dégradation des briques des poches de coulée a été établie d'après les caractéristiques microstructurales, chimiques et physiques.

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INTRODUCTION

Atlas Steels Company, Welland, Ontario, is cooperating with CANMET in the conduct of evaluation of the mechanisms of wear of refractories used to line steelmaking vessels. Currently, pursuant to previous work at CANMET, they are conducting plant trials in which dolomite refractories are substituted for the chrome/magnesia bricks previously used: results to date indicate that dolomite has extended the service life of the linings to circa 40 heats.

However, some anomalous results have been observed with some of the other refractories used in the composite ladle linings. Aluminosilicate refractories, 70% alumina, are used in the pad area of the ladle wall subject to impact and erosion by the metal stream during charging of the ladle. Six-inch thick bricks used for the purpose usually gave service of up to 40 heats. To ensure balanced wear, 7-inch bricks of the same nominal composition and properties were substituted in the pad area. Unexpectedly, these bricks showed severe erosion in only 9-15 heats; wear apparently originated at the joints. An investigation to seek the causes of this anomalous behaviour was undertaken at CANMET under the project "Electrodes and Refractories for Steelmaking".

EXPERIMENTAL PROCEDURES

MATERIALS

The following samples were provided by Atlas Steels:

One 7" Universal Circle Brick: 7-30 SU, 70% Al_2O_3,
One 6" Universal Circle Brick: 6-30 SU, 70% Al_2O_3,
One fragment of a used 7-inch brick (7-30SU).

For laboratory slagging tests, a sample of VAD slag on hand from previous work was used. The composition is given in Table 1.

MICROSTRUCTURAL STUDIES

Both polished and thin sections of the materials were prepared. Optical (OM) and scanning electron microscopy (SEM) were used to examine the microstructural characteristics of the used and unused bricks. Compositional variation of the used and unused bricks was determined qualitatively by means of energy dispersive X-ray analysis (EDXA). In addition, X-ray diffraction (XRD) was used as an aid for phase identification.

SLAG CORROSION TEST

Slag resistance of the two different size refractories was examined by the cup test technique. In this test, cylindrical blocks of approximately 3.6 cm in diameter by 3.6 cm high were machined from the bricks. A hole of 1.3 cm diameter by 3 cm deep was core drilled at the center of the cylinder. Five grams of slag having the composition shown in Table 1 were packed into the refractory cup. The cup and its contents were then loaded into a molybdenum safety crucible, which was in turn placed in the vacuum furnace. Following the evacuation of the furnace to a pressure of approximately 0.25 Pa, the temperature of the furnace was increased rapidly to 1700°C and held for three hours. The test sample, after cooling to room temperature, was sectioned so that the degree of slag corrosion could be visually and optically examined.

SOFTENING TEST

Pyrometric cones were prepard from representative aliquots of the two unused bricks, according to ASTM Test Method C-24. The Pyrometric Cone Equivalent (specific softening or deformation temperature) was found to be beyond the capabilities of CANMET's PCE furnace. As a result, the extent of difference in the softening temperature of the cones made from these bricks was examined in the vacuum furnace at temperatures between 1850 and 1950°C.

ABSORPTION TEST

The water absorption of the two different bricks was determined according to ASTM Test Method C-20.

RESULTS AND DISCUSSION

BULK PHYSICAL PROPERTIES

Megascopically, the principal visible difference between the unused bricks is the relative amounts of the grog grains, which range from grey to brown to violet and are randomly distributed in the yellowish matrices. Sections across the bricks reveal that the 7" brick contains appreciably more grog and fewer "islands" of dense, fine-grained, grog-free material that forms the bond phase.

Some bulk properties, determined on representative samples from the two batches of bricks, were reported by Atlas Steels:

	6-inch bricks	7-inch bricks
Bulk Density (g/mL)	2.62	2.56-2.60
Total Porosity (%)	18.8-18.9	19.1-20.0
Water Absorption (%)	6.9	7.7

The water absorptions were determined at CANMET on duplicate samples cut from a single brick: the values reflect that part of the porosity that would be most readily penetrated by molten slag.

The most likely explanation for the greater porosity/absorption of the 7-inch bricks lies in their greater grog content. As the grog is pre-fired, it will show little if any firing shrinkage, whereas the bond phase will sinter and shrink: this differential shrinkage, if sufficiently large, can lead to microcracking in the matrix adjacent to the grog grains, with the number of microcracks proportional to the number of grog grains.

However, in our opinion, a difference of only up to 1% in porosity/absorption, although it may be a contributing factor, is unlikely to make a principal contribution to the reduced service life.

The dimensional accuracy of the samples supplied to CANMET was verified: the lengths and heights were closely similar. With the two bricks accurately juxtaposed, a difference in length of probably several micrometres was evident by feel, the 7-inch brick being shorter. No difference in height was evident in the same circumstances. In view of the fact that brick erosion appears to be joint-related it is recommended that this parameter be examined further in terms of a representative sample of the two batches of bricks involved.

BEHAVIOUR IN STEELMAKING ENVIRONMENTS

The mechanisms of corrosion of the bricks in contact with slag were examined through microstructural analysis of unused and used bricks.

Unused Bricks

The principal visible difference in the unused bricks lay in the proportions of grog, which itself comprised three apparently different types (based on colour) that were observed in cut sections to be non-uniformly distributed. These apparently different grog types were examined microscopically. The gray grains are composed of subhedral to euhedral mullite and alumina in a fine-grained matrix (Fig. 1). Lath-shaped to anhedral grains are commonly observed in the brown grog grains, as shown in Fig. 2. The violet grog grains are composed predominantly of crystals of mullite and alumina, which are bonded tightly by an interstitial phase (Fig. 3). The difference in composition cannot be considered substantial.

Typical microstructures of the two unused bricks are given in Fig. 4 and 5, along with EDXA maps showing distribution of the principal elements present. The microstructures are closely similar: grains of mullite/alumina grog (compositions confirmed by XRD) are distributed in a highly aluminous matrix. The elemental distribution maps for silica show a minor amount of discrete silica grains at the mullite-alumina grain boundaries within the 7-inch bricks, which were not observed in the 6-inch brick. This difference is not considered of major significance in light of the closely similar refractoriness of the two materials demonstrated by the comparative cone deformation test: at 1950°C neither cone was fully deformed but, based on experience, the difference in pyrometric cone equivalent temperature is estimated at no more than 10°C, the 7-inch brick being slightly the less refractory. This result confirms the very close similarity of the bricks in terms of chemical and mineralogical composition.

It is assumed from the fired compositions that the original raw materials of the bond phase, and at least most of the grog, comprised clay and alumina. On calcining the grog and again on firing the bricks, the clay ($Al_2O_3.2SiO_2.2H_2O$) dehydroxylates at lower temperature and the resultant amorphous mixture of alumina and silica recombines at high

temperature to form mullite ($3Al_2O_3.2SiO_2$), precipitating free silica. In the presence of excess alumina, this fine-grained, reactive silica would be expected to react to form more mullite, as can be assumed the case for the 6-inch bricks in which no free silica was observed microscopically or detected by XRD. Possible explanations may be postulated for the presence of silica: a) insufficient alumina in the 7-inch brick to react with the silica; this seem unlikely as the stated composition (70% Al_2O_3) would indicate an excess of alumina, borne out by the microstructural and refractoriness evidence given above; b) non-uniform distribution of the alumina (alumina-silica contact is necessary for reaction in the solid state to form mullite); there is some evidence to support this, much of the alumina is present in the large grog grains (which are less reactive) and there is appreciably more grog in the 7-inch brick; c) firing of the 7-inch bricks at lower temperature (or at peak temperature for a shorter time), i.e., an insufficient heat treatment for the mullitization reaction to proceed to completion; this possibility is supported by the greater porosity of the 7-inch bricks (consistent with a lesser heat treatment) and by the fact that occasional silica crystallites were observed in direct contact with large (but therefore poorly reactive) alumina grains, but does not appear to be consistent with the apparent size data.

On the other hand, in ladle service this fine-grained (and hence highly reactive) silica in some of the grain boundaries would be expected to react readily with penetrating slag at high temperatures, which could contribute to earlier failure of the 7-inch brick. However, the content of free silica is so small that it is considered unlikely to be a major factor in degradation of the bricks.

Used Bricks

Megascopically, the used brick from the ladle is grey to dark grey. At the slag-brick interface, it is composed of a dense layer of lath-shaped crystals grading into a layer of less dense material containing numerous pores. Photomicrographs of the used brick are given in Fig. 6 and 7, illustrating that it is composed of mainly lath-shaped to dendritic shaped crystals with slag-filled interstices. An SEM micrograph of the slag/brick interface is given in Fig. 8, along with EDXA maps of the distribution of the elements detected. The lath-shaped crystals are composed of alumina

and/or alumina and silica, confirmed to be α-alumina and mullite respectively by XRD. The interstitial materials are calcium alumino-silicates, identified by XRD as gehlenite and anorthite.

For comparison, slagging tests were conducted in the laboratory, using cups cut from the two unused sample bricks. Sections at the slag/brick interface for 7-inch and 6-inch bricks respectively, reacted at 1650°C for 3 hours, are given in Fig. 9 and 10. No perceptible difference could be noted in the extent of slag penetration or degree of reaction. In both cases, the microstructures are characterized by lath-shaped alumina crystals scattered in the slag. Some of the grog grains are less susceptible to attack and remain intact, forming islands in the slag. In general, it appears that the mullite phase is attacked by the slag to form low-melting calcium aluminosilicates, and the excess alumina recrystallizes as euhedral to subhedral crystals. Thus, the laboratory tests confirm the behaviour noted in the used brick: the greater degree of reaction observable in the used brick from the ladle is considered to be a function of repeated attack over several heats.

CONCLUSIONS

1) The bulk properties of the 6-inch and 7-inch bricks are closely similar: their differences may reflect no more than the normal temperature gradients in the kiln(s) in which they were fired. The slightly greater porosity observed for the 7-inch brick may be a minor contributor to their shorter service life.

2) Megascopically, the 7-inch brick sample contains more grog than the 6-inch brick. As near as can be determined visually, the proportions of the three types of grog (identified by colour) are closely similar within the two types of brick. As the grog is usually more refractory than the matrix bond phase in refractories, this would not normally contribute to reduced service life. The refractoriness of the two sizes of bricks, as determined by cone deformation, is nearly identical, indicating nearly identical chemical and mineralogicalover-all compositions.

3) Both optical and SEM microscopy indicate that the microstructures of the two sizes of bricks are essentially identical. The only notable difference is the presence of a small amount of free silica observed in some of the grain boundaries of the 7-inch brick sample only. This silica is presumed to have originated during the mullitization of the original components of the grog and/or bond phase. Although these fine crystallites of silica could be expected to dissolve readily in penetrating slag, they are present in such small quantity and are so widely dispersed over the microstructure that they are considered unlikely to be a major factor contributing to degradation of the bricks.

4) No differences were found in the reactions of the bricks and slag at high temperatures. The used brick, after service in the ladle, showed the same reaction products as did both bricks in the laboratory cup tests. In each case, the molten slag primarily caused decomposition of the mullite phase to form calcium aluminosilicates, with the excess alumina recrystallizing. The greater extent of reaction in the brick from the ladle is attributed to longer exposure time, during several heats. There was no perceptible difference in the depth of slag penetration and/or of reaction in the cups of 6-inch and 7-inch bricks.

5) In view of the observation that the degradation of the bricks originated at the joints, some further examination of brick sizes is recommended. The 7-inch brick sample supplied to CANMET was slightly, but perceptibly shorter than the 6-inch brick. If this is found to be generally true for the batch, it would lead to more-open joints, in turn more susceptible to slag penetration and corrosion/erosion. In this event, one solution would be to use a dip-joint of fine-grained high-alumina mortar when laying the bricks in the ladle.

If the 7-inch bricks are indeed shorter, there remains an unexplained anomaly. The 7-inch bricks visibly contain more grog, which has had its firing shrinkage at least largely removed during calcination; thus they could be expected to be oversize. Similarly, if the 7-inch bricks had been afforded a lesser heat treatment during firing, which is consistent with their greater porosity and is also one postulated reason for the presence of unreacted silica, they could again be expected to be oversize. Reasons

for this incongruity may arise from the manufacturing process, e.g., different lengths of forming dies, differences in drying and firing schedules.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the contributions of G. Lemieux, Ceramic Section, who conducted most of the tests, and of D. Owens, Mineralogy Section, who performed the SEM and EDXA work.

Table 1. Composition of the slag used for the cup tests

CaO	60.06%
MnO	0.06
SiO_2	19.20
Cr_2O_3	0.02
Al_2O_3	7.68
MgO	3.69

Fig. 1. Microstructure of a typical grey grog grain

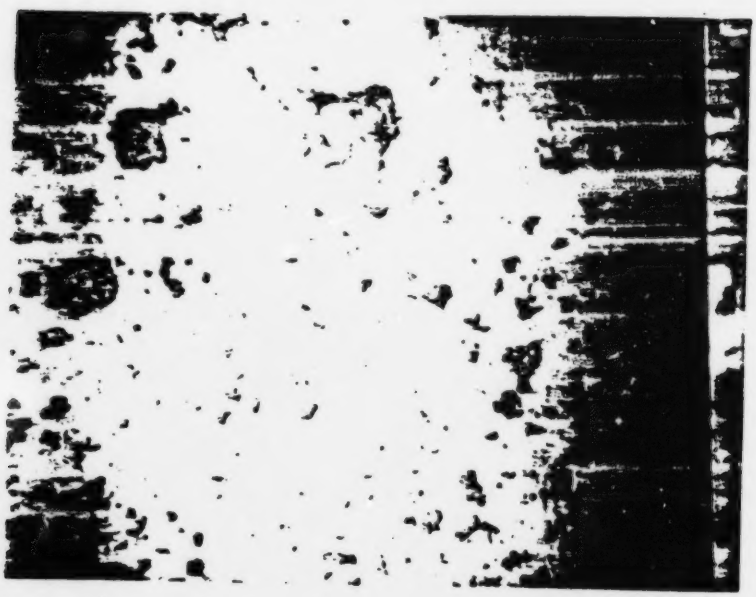

Fig. 2. Microstructure of a typical brown grog grain

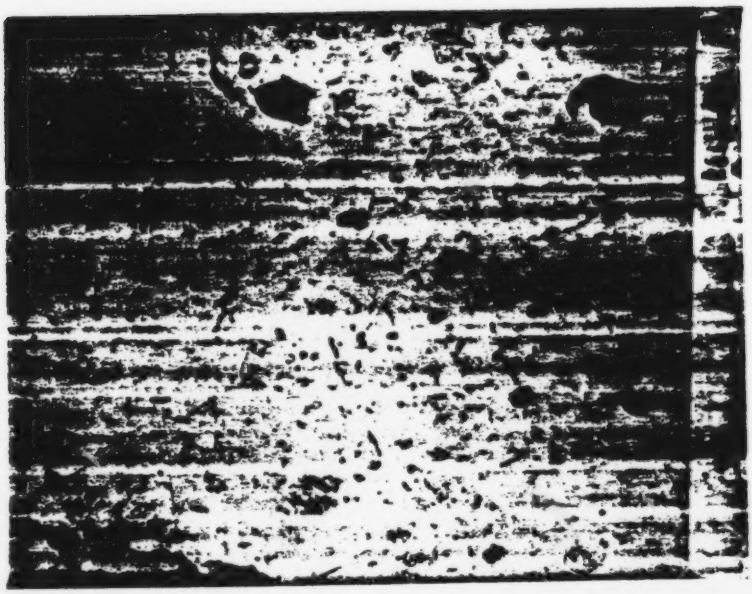

Fig. 3. Microstructure of a typical violet grog grain

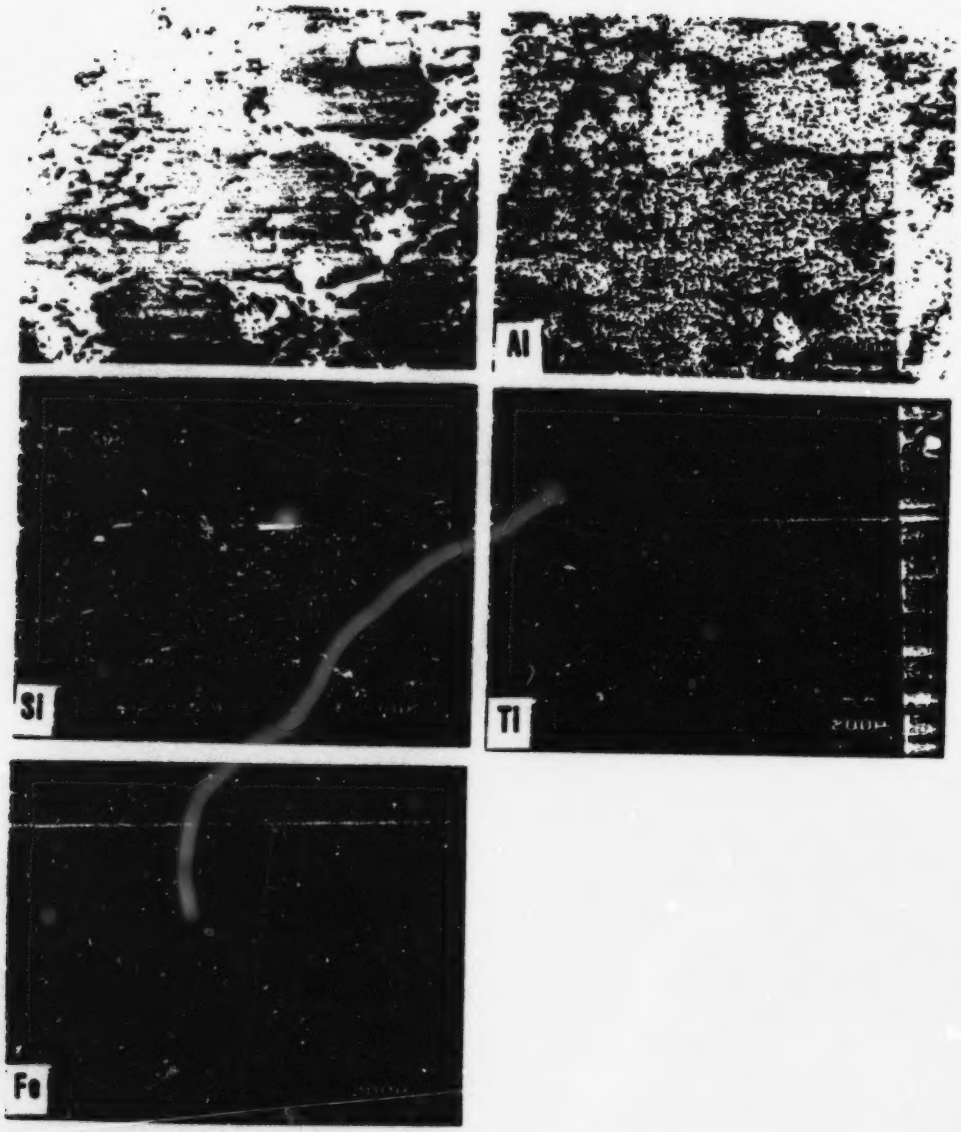

Fig. 4. SEM micrograph and elemental distribution maps for Si, Al, Ti and Fe of the unused 7-inch brick

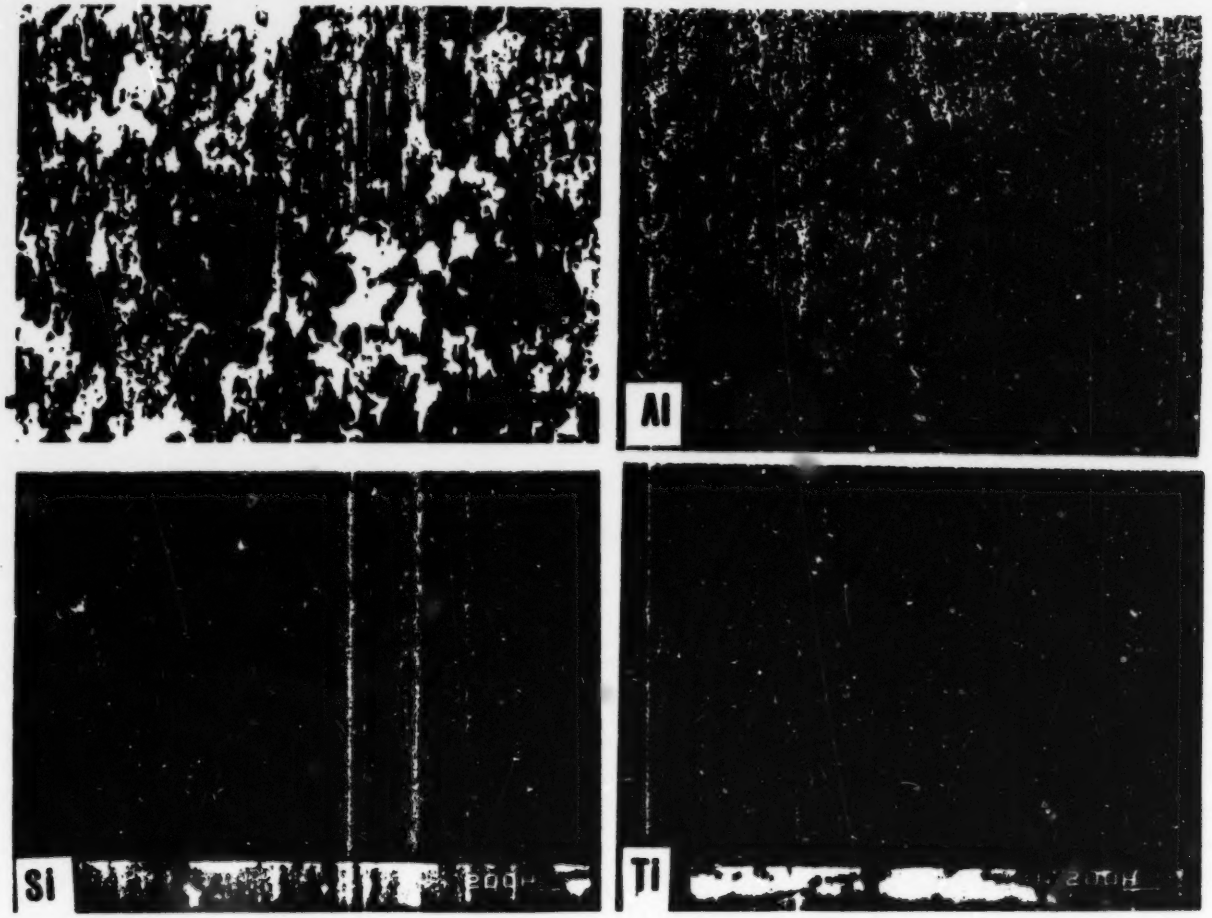

Fig. 5. SEM micrograph and elemental distribution maps for Si, Al and Ti of the unused 6-inch brick

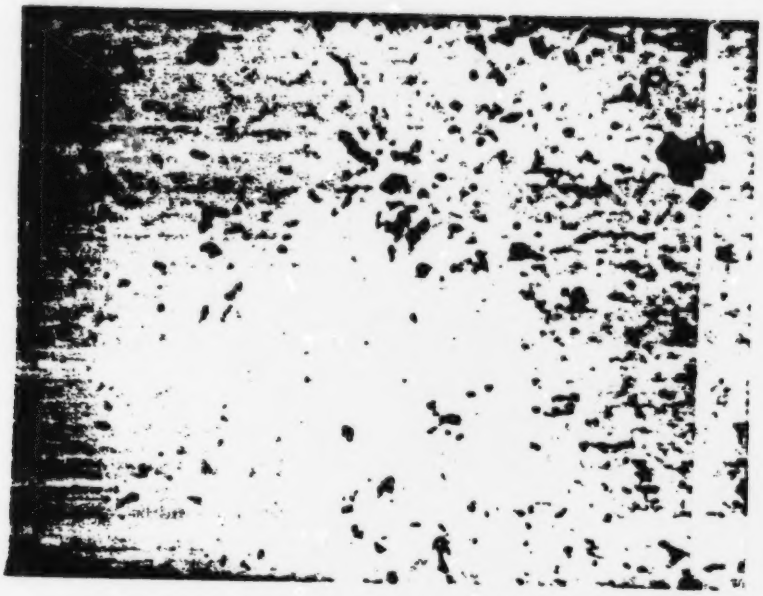

Fig. 6. Microstructure of used brick from the ladle

Fig. 7. Microstructure of used brick from the ladle

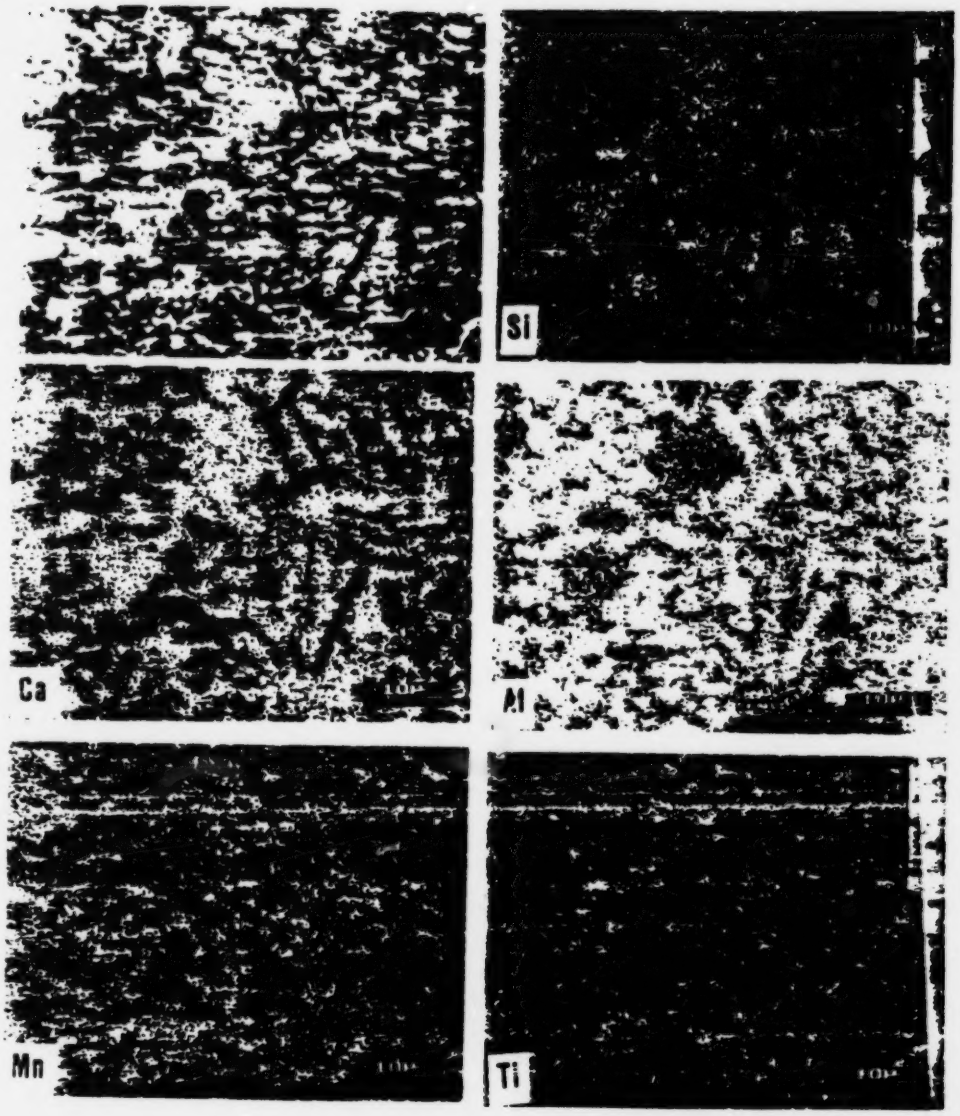

Fig. 6. SEM micrograph and elemental distribution maps for Ca, Mn, Si, Al and Ti at the slag-brick interface of a used brick from the ladle

Fig. 9. Microstructure of the 7-inch brick at the slag-cup interface

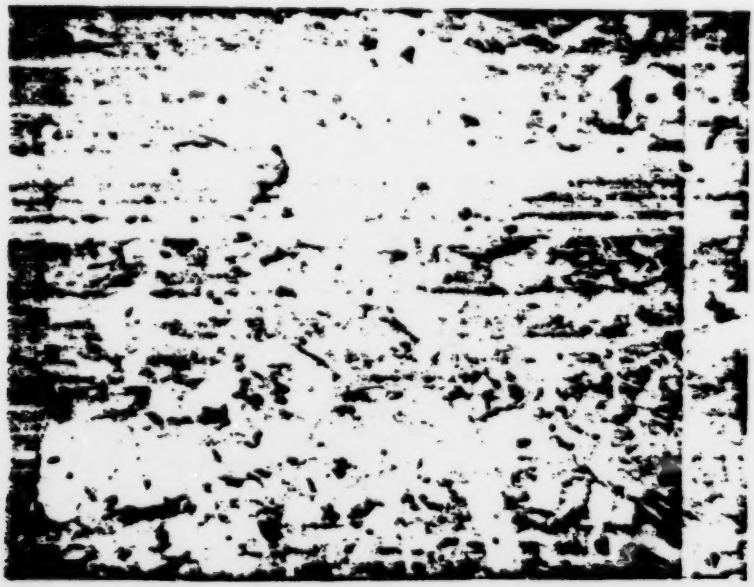

Fig. 10. Microstructure of the 6-inch brick at the slag-cup interface